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Note

KINETIC PARAMETERS OF THE THERMOGRAVIMETRIC DISSOCIATION OF PRIMARY ALIPHATIC AMINE COMPLEXES DERIVED FROM TETRAQUOCOPPER(II)NITROSOPENTACYANOFERRATE(II)

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Tetraquocopper(II)nitrosopentacyanoferrate(II) forms $|Cu(am)(H_2O)_3|$ $|Fe(CN)_5NO| \cdot H_2O$-type complexes, where am = methyl-, ethyl-, propyl-, butyl- and amylamine: these complexes have already been characterised by the authors elsewhere. All complexes contain one molecule of lattice water, three molecules of coordinated water and one molecule of amine. Thermogravimetric analysis indicates that cation dissociation is followed by anion dissociation. Kinetic parameters, e.g. rate of reaction, order of reaction and apparent energy of activation, have been determined. Energy of activation values show that the coordinated water is slightly weaker than the coordinated amine ligand.

INTRODUCTION

Recently, some work has been done on the thermogravimetric analysis of simple amine complexes of transition metals but complexes of the type under investigation where both cation and anion are complexes have not been studied in detail [1–5].

Many methods have been developed for deriving kinetic data from thermogravimetric curves [6–8]. Of these, the best method for the computation of thermogravimetric data gives the rate constant and energy of activation values from plots of $|-\ln(1-\alpha)|^{1/n}$ vs. time and $\{-\ln[-\ln(1-\alpha)]^{1/n}\}/T^2$ vs. $1000/T$ for $n = 1$.

EXPERIMENTAL

Thermogravimetric analysis was performed on a thermobalance supplied by Fertiliser Corporation of India. Mass loss data was obtained at a heating

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TABLE 1

Complex	Temp. (K)	Weight loss		Gaseous product	Energy of activation		Rate of reaction (min^{-1})
		Obs.(%)	Calcd.(%)		(kcal ($mole^{-1}$)	(kJ $mole^{-1}$)	
1. $|Cu(CH_3NH_2)(H_2O)_3|$ $|Fe(CN)_5NO|\cdot H_2O$	273– 953	67.01	68.78				
	333– 413	4.49	4.71	H_2O lattice	11.00	45.98	2.52×10^{-1}
	413– 543	15.34	14.12	3 H_2O coordinated	12.42	51.91	9.55×10^{-2}
	543– 573	7.37	8.11	CH_3NH_2	18.40	76.91	3.89×10^{-2}
	573– 593	6.35	7.84	NO	11.03	46.10	1.86×10^{-2}
	593– 953	35.45	34.00	5 CN	149.33	620.02	5.40×10^{-3}
2. $|Cu(C_2H_5NH_2)(H_2O)_3|$ $|Fe(CN)_5NO|\cdot H_2O$	273– 953	68.75	69.88				
	333– 383	4.35	4.54	H_2O lattice	9.83	41.08	3.77×10^{-1}
	383– 533	13.87	13.63	3 H_2O coordinated	11.13	46.52	1.44×10^{-2}
	533– 573	12.31	11.35	$C_2H_5NH_2$	18.07	75.53	1.25×10^{-2}
	573– 598	6.87	7.57	NO	11.82	49.40	1.45×10^{-1}
	598– 953	31.35	32.80	5 CN	143.38	599.32	5.02×10^{-3}

3. $|Cu(C_3H_7NH_2)(H_2O)_3|$	273– 953	66.96	70.90				
$|Fe(CN)_5NO|\cdot H_2O$	333– 393	4.28	4.38	H_2O lattice	9.93	41.50	2.64×10^{-1}
	393– 473	11.40	13.15	3 H_2O coordinated	11.55	48.27	1.23×10^{-1}
	493– 563	13.90	14.38	$C_3H_7NH_2$	14.42	60.27	3.50×10^{-2}
	573– 593	6.48	7.31	NO	10.33	43.17	1.35×10^{-2}
	593– 953	30.90	31.68	5 CN	144.05	602.13	3.63×10^{-2}
4. $|Cu(C_4H_9NH_2)(H_2O)_3|$	273–1053	68.71	71.85				
$|Fe(CN)_5NO|\cdot H_2O$	333– 393	4.73	4.25	H_2O lattice	8.95	37.53	2.6×10^{-2}
	393– 513	11.19	12.72	3 H_2O coordinated	10.39	43.43	9.77×10^{-2}
	513– 573	15.92	17.20	$C_4H_9NH_2$	17.38	72.68	2.16×10^{-2}
	573– 593	6.12	7.06	NO	11.09	46.35	2.01×10^{-2}
	593–1053	30.44	40.49	5 CN	149.25	626.37	5.20×10^{-3}
5. $|Cu(C_5H_{11}NH_2)(H_2O)_3|$	273–1013	69.12	72.76				
$|Fe(CN)_5NO|\cdot H_2O$	333– 433	4.33	4.10	H_2O lattice	8.87	37.07	3.65×10^{-1}
	433– 513	11.68	22.31	3 H_2O coordinated	9.48	39.63	1.355×10^{-2}
	513– 573	17.61	19.85	$C_5H_{11}NH_2$	16.68	69.72	3.39×10^{-2}
	573– 593	6.61	6.85	NO	11.90	49.99	1.84×10^{-2}
	593–1013	29.43	29.66	5 CN	148.01	618.68	5.48×10^{-3}

rate of 10°C $\min^{-1}$ up to 1073 K. The observed and calculated values are given in Table 1.

RESULTS AND DISCUSSION

The rate of thermal dissociation of a complex was determined from the rate at one or more stages; the mid point of thermal decomposition was taken for rate constant determination for any individual reaction [9]. Above 573 K, similar plots were obtained for all the five complexes studied but the plots were slightly different in the range 293–573 K. Representative plots of the complex $|Cu(CH_3NH_2)(H_2O)_3||Fe(CN)_5NO| \cdot H_2O$ are given in Figs. 1 and 2. Values of α were calculated from mass-loss data using the expression $\alpha = (w_t - w_f)/(w_0 - w_f)$, where w_t = mass at time/temperature, w_0 = initial sample mass, and w_f = residual mass at the end of the process under study.

The results of thermogravimetric analysis clearly distinguish the various thermal reactions occurring over different ranges of temperature. All the five complexes contain one molecule of lattice water and three molecules of coordinated water. Thermal decomposition begins with weight loss at 333 K resulting from the loss of the lattice-water molecule. The deaquation of lattice water is completed at 413, 383, 393, 393 and 433 K in complexes 1–5 (as listed in Table 1), respectively. This stage is indicated by the presence of a break in the thermogravimetric curve. The deaquation of the three coordinated water molecules in all the complexes begins after deaquation of the lattice water molecule and is completed at 543, 533, 473, 513 and 513 K in complexes 1–5, respectively. As expected, the energy of activation of coordinated water is higher than that of lattice water.

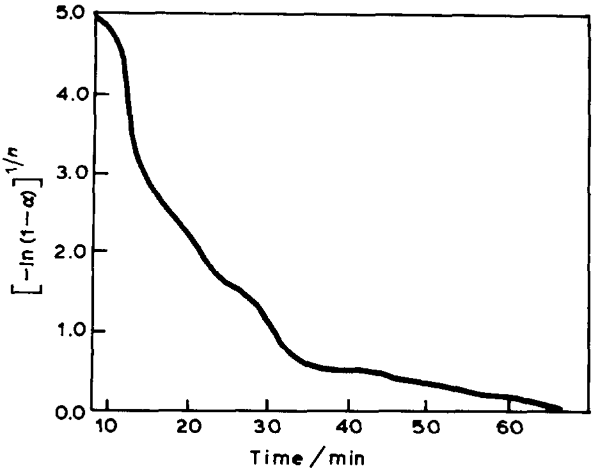

Fig. 1. $[-\ln(1-\alpha)]^{1/n}$ vs. time for $[Cu(CH_3NH_2)(H_2O)_3][Fe(CN)_5NO] \cdot H_2O$ with $n = 1$.

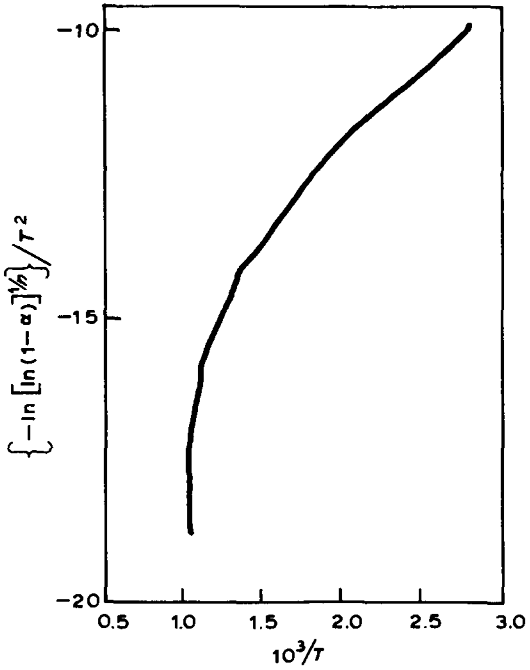

Fig. 2. $\{-\ln[\ln(1-\alpha)]^{1/n}\}/T^2$ vs. $10^3/T$ for $[Cu(CH_3NH_2)(H_2O)_3][Fe(CN)_5NO]\cdot H_2O$ with $n = 1$.

Deamination begins at 543, 533, 493, 513 and 513 K and is completed at 573, 573, 563, 573 and 573 K in complexes 1–5, respectively, corresponding to loss of methyl, ethyl, propyl, butyl and amylamine. The temperature at which deamination occurs shows that the strength of the amine ligand decreases on going from methylamine to amylamine because of the increase in the bulky nature of the amine series. The strength of the Cu–N bond, therefore, decreases as the molecular weight of the amine increases. The absence of any horizontal plateau in the thermogravimetric curve also indicates that the decomposition of coordinated water and amine overlap.

At 573, 573, 563, 573 and 573 K the decomposition of the cation portion of the complexes is complete for complexes 1–5, respectively. At these temperatures a small break is observed in the thermogravimetric curves of all the complexes as the anion portion of the complexes, viz. $|Fe(CN)_5NO|$ starts to decompose. First, the NO group is evolved, as indicated by the appearance of brown fumes, followed by the decomposition of CN groups. At the end of the complete decomposition of the complexes, a black residue is obtained probably of metal carbide and nitride. All the reactions have been found to be of the first order.

To conclude, the ligands can be arranged in order of their increasing strength in the spectrochemical series as: H_2O lattice < H_2O coordinated < $C_5H_{11}NH_2 < C_4H_9NH_2 < C_3H_7NH_2 < C_2H_5NH_2 < CH_3NH_2 < NO < CN$.

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